

*Citation for published version:*

Williamson, DL, Herdes, C, Torrente-Murciano, L, Jones, MD & Mattia, D 2019, 'N-Doped Fe@CNT for Combined RWGS/FT CO<sub>2</sub> Hydrogenation', *ACS Sustainable Chemistry and Engineering*, vol. 7, no. 7, pp. 7395-7402. <https://doi.org/10.1021/acssuschemeng.9b00672>

*DOI:*

[10.1021/acssuschemeng.9b00672](https://doi.org/10.1021/acssuschemeng.9b00672)

*Publication date:*

2019

*Document Version*

Peer reviewed version

[Link to publication](#)

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# N-doped Fe@CNT for combined RWGS/FT CO<sub>2</sub> hydrogenation

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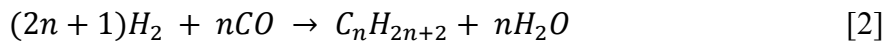
ABSTRACT: Conversion of CO<sub>2</sub> into chemical fuels represents an attractive route for green house gas (GHG) emissions reductions and renewable energy storage. Iron nanoparticles supported on graphitic carbon materials (e.g. carbon nanotubes) have proven themselves to be effective catalysts

for this process. This is due to their stability and ability to support simultaneous reverse water gas shift and Fischer-Tropsch catalysis. Typically, these catalytic iron particles are post-doped onto an existing carbon support via wet impregnation. Nitrogen doping of the catalyst support enhances particle-support interactions by providing electron-rich anchoring sites for nanoparticles during wet impregnation. This is typically credited for improving CO<sub>2</sub> conversion and product selectivity in subsequent catalysis. However, the mechanism for RWGS/FT catalysis remains underexplored. Current research places significant emphasis on the importance of enhanced particle-support interactions due to N-doping, which may mask further mechanistic effects arising from the presence or absence of nitrogen during CO<sub>2</sub> hydrogenation. Here we report a clear relationship between the presence of nitrogen in the CNT support of a RWGS/FT iron catalyst, and significant shifts in the activity and product distribution of the reaction. Particle-support interactions are maximized (and discrepancies between N-doped and pristine support materials minimized) by incorporating iron and nitrogen directly into the support during synthesis. Reactivity is thus rationalized in terms of the influence of C—N dipoles in the support upon the adsorption properties of CO<sub>2</sub> and CO on the surface, rather than improved particle-support interactions. These results show that the direct hydrogenation of CO<sub>2</sub> to hydrocarbons is a potentially viable route to reduce carbon emissions from human activities.

**KEYWORDS:** CO<sub>2</sub>, catalysis, nitrogen, doping, iron, carbon nanotube, hydrocarbon, water gas shift, Fischer-Tropsch, storage, adsorption, simulation

## **INTRODUCTION:**

The water gas shift (WGS) [1] and Fischer-Tropsch (FT) [2] processes have long been used in industry for hydrogen and hydrocarbon formation.<sup>1-8</sup>



However, to mitigate CO<sub>2</sub> emissions and cope with the intermittent supply patterns of renewable energy sources, research has been increasingly focused on converting CO<sub>2</sub> into hydrocarbon fuels. This could allow for energy storage directly from CO<sub>2</sub> and excess renewable energy.<sup>9-14</sup> Coupling the reverse water gas shift (RWGS) and FT reactions together into a single process is considered to be especially desirable.<sup>15</sup> Simultaneous consumption of CO produced by RWGS via subsequent FT catalysis shifts the equilibrium of the RWGS reaction towards products, enhancing the overall efficiency of the process.<sup>16-17</sup>

Iron-based catalysts are particularly amenable to this process, as the high temperature RWGS reaction is catalyzed by promoted iron oxides,<sup>1, 18-20</sup> and the Hägg carbide is active in FT catalysis.<sup>11, 21-25</sup> Iron nanoparticles supported on carbon nanotubes (often referred to as Fe-CNT or Fe/CNT type catalysts) have proven themselves to be active catalysts for this coupled process due to their stability, adsorption capacity, and ability to support the active species of both reactions.<sup>26-27</sup> It has also been shown that increasing interactions between the catalytic nanoparticles and the CNT support is critical to achieve high activity in Fe/CNT catalysts. Catalysts where the iron particles have been integrated into the CNT support directly during synthesis (Fe@CNT) are significantly more active than catalysts where particles have been doped onto the CNT support in a separate step.<sup>15, 26, 28-35</sup>

Functionalisation of the CNT support has been explored in recent years as a means of enhancing these particle-support interactions.<sup>11, 36-37</sup> Nitrogen incorporation leads to improved conversion, reducibility and particle dispersion, which has been attributed to increased overlap between the metal 3d orbitals and excess  $\pi$ -electron density in the graphitic plane.<sup>11, 36, 38-40</sup> However, studies

until this point have focused exclusively on the effect of nitrogen doping in pure FT synthesis, or have only investigated catalysts where the nitrogen and iron nanoparticles have been post-doped onto an existing CNT support separately.<sup>11, 36</sup> This limits interactions between the three key components of the catalyst, and makes it difficult to draw conclusions regarding the isolated mechanistic effects arising from the presence or absence of nitrogen in the support during CO<sub>2</sub> hydrogenation. In these instances, nitrogen doping is certain to affect the intrinsic activity of the catalyst significantly by influencing particle dispersion on the support, and the magnitude of support-particle interactions once the particles are deposited.<sup>11, 36, 39, 41</sup>

In this work we aim to elucidate the influence of nitrogen doping of graphitic carbon nanotube supports for CO<sub>2</sub> conversion catalysis by enhancing the magnitude of (and reducing the discrepancy between) particle-support interactions in Fe/CNT- and Fe/NCNT-type catalysts. Here we report the clearest comparison yet between the reactivity of cohesive Fe@CNT and Fe@NCNT in combined RWGS/FT catalysis for CO<sub>2</sub> hydrogenation, where iron and nitrogen have both been incorporated into the catalyst directly during CVD synthesis. This provides the most thorough possible integration between all elements of the catalyst and offers insights into the effect of nitrogen doping on the overall CO<sub>2</sub> hydrogenation process through combined characterization, catalytic testing and molecular dynamics simulations.

## **EXPERIMENTAL:**

**Catalyst synthesis** was achieved as follows: To produce Fe@CNT, 1.0 g ferrocene (FcH) was dissolved in 50 mL toluene to produce a CVD precursor solution of concentration 20 mg mL<sup>-1</sup> FcH in toluene. 40 mL of the precursor solution was then injected at a rate of 10 mL h<sup>-1</sup> into a quartz tube (25 mm ID x 28 mm OD x 122 cm L), loaded in a tubular furnace at 790 °C under a flow of 50 sccm H<sub>2</sub> and 400 sccm Ar. After 4 hours of CVD injection, the raw catalyst was readily

retrieved from within the quartz tube by scratching the interior cavity of the quartz tube with an elongated spatula. A 40 mL injection synthesis typically yielded ca. 1.5 g of catalyst. To produce Fe@NCNT, the same procedure was employed while replacing toluene in the precursor solution with acetonitrile (ACN) to act as a source of both carbon and nitrogen during the CNT growth process. To minimize error due to variance between catalyst batches, a stock of ca. 10 g was produced before beginning catalytic trials, and topped up every 3 reactions. 0.5 wt. % Na doping was achieved in Na-Fe@NCNT via wet impregnation. 9 mg NaHCO<sub>3</sub> (Sigma-Aldrich, 99.7%) was dissolved in 15 mL deionized water with 0.5 g Fe@NCNT. The slurry was stirred for 24 hours and subsequently heated at 115 °C for 2 hours before collecting the dried powder.

**Catalysts activation** was achieved by loading 0.47 g of the into a stainless steel calcination tube (0.5 inch OD x 0.451 ID x 6 inch L). This tube was plugged at one end with quartz wool (9-30 micron, H. Baumbach & Co Ltd) to prevent the catalyst from escaping while still allowing for air flow. For Fe@ NCNT-based materials, the tube was then heated in a muffle oven at 400 °C for 1 hour under a static air atmosphere, with a heating ramp rate of 10 °C min<sup>-1</sup>. For any Fe@CNT-based materials, the same process was repeated, though the catalysts were instead heated to 570 °C for 40 min. Further information on the origin of these different activation temperatures can be found in the ESI.

**CO<sub>2</sub> conversion testing** was conducted by loading 0.4 g of the desired catalyst into a stainless steel reaction tube (0.5 inch OD x 0.451 inch ID x 6 inch L), which was plugged with quartz wool (9-30 micron, H. Baumbach & Co Ltd) at both ends to ensure that the catalyst powder rested securely in the middle of the tube. The sample was then placed in a tubular furnace and heated to 400 °C for 3 hours under a flow of 50 sccm H<sub>2</sub> to reduce the catalyst. To begin the combined RWGS/FT process, the temperature was lowered to 370 °C and the was pressure gradually raised

to 15 bar while maintaining the desired reaction gas ratio (3:1 H<sub>2</sub>:CO<sub>2</sub>). A high overall flow rate (180 sccm) was employed during this step to facilitate pressurization of the reactor. When the desired pressure had been achieved, the flow rate was lowered to the reaction flow rate of 8 sccm. The reactor was left for 2 hours to equilibrate following pressurization, after which samples were taken hourly for 3 hours via a 50 mL SGE gas tight syringe with leur-lock fittings and analyzed via GC-MS. An Agilent Technologies 7890A GC System with Agilent Technologies 5975C insert MSD with Triple-Axis Detector (MS, TCD, FID) was used as the GC-MS instrument. The installed column was an HP-Plot Q column. The TCD was used to quantify CO<sub>2</sub> and CO, while the FID was used to quantify hydrocarbon species. 1% Ar in H<sub>2</sub> was used as the source in CO<sub>2</sub> conversion experiments so that Ar could be used as an internal standard during GC-MS measurements.

It should be noted that the chosen reaction conditions have been previously identified as producing noteworthy CO<sub>2</sub> and CO conversion over Fe@CNT-type materials.<sup>15</sup> However, the stated flow rate of 8 sccm should be considered low for the tested catalyst powder mass of 0.4 g. Diffusion limitations may play a role in masking the intrinsic activity of the catalyst and conditions at the catalyst surface. Further work must be conducted to optimize the reaction process.

**Catalyst characterization** was achieved with Raman, TEM, XPS, XRD, and TPD. Raman analysis was conducted using a Renishaw InVia system with a 532 nm laser. For CNT-based materials, a laser power of 5% was employed with the standard exposure time to facilitate quick analysis without burning or damaging the sample during analysis. For NCNT-based materials, the laser power was reduced to 0.1% due to the decrease in the stability of the CNT lattice caused by nitrogen doping leading to significant decomposition under even 1% laser power. Consequently, the exposure time for NCNT-based samples was also increased substantially to 400 seconds to

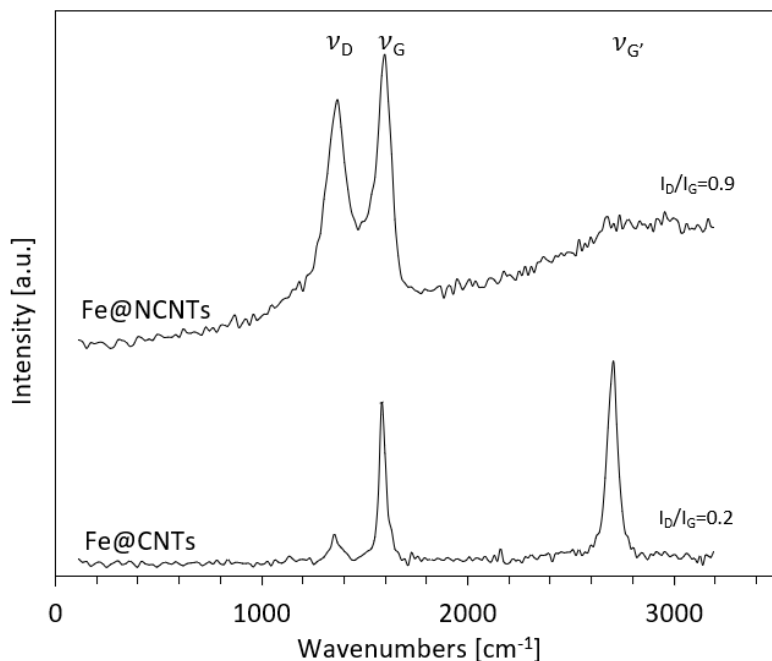
collect a clear Raman spectrum. TEM analysis was conducted using a JEOL JSM-2100PLUS at an accelerating voltage of ca. 200 kV. Particle and tube diameters were measured using the open source image processing package Fiji. XPS analysis was conducted using a Kratos Axis Ultra-DLD system. Samples were analyzed using a micro-focused monochromatic Al X-ray source (72 W) over an area of approximately 400 microns. Data was recorded at pass energies of 150 eV for survey scans and 40 eV for high resolution scan with 1 eV and 0.1 eV step sizes respectively. Charge neutralization of the sample was achieved using a combination of both low energy electrons and argon ions. XRD analysis was conducted using a Bruker D8 Advance with Vantec Detector using Cu K- $\alpha$ 1 radiation was used to analyze all samples, which were scanned in flat plate mode from 20-80° at a scan rate of 0.27° min<sup>-1</sup> (4 hours per sample). H<sub>2</sub>, CO and CO<sub>2</sub> TPD analysis were conducted using a Micrometrics AutoChem II 2920 V4.03 Automated Catalyst Characterization System with Thermal Conductivity Detector (TCD). Samples were subjected to temperature programmed reduction up to 1000 °C at 10 °C min<sup>-1</sup> (50 sccm 5% H<sub>2</sub> in Ar), pulse chemisorption of the desired analysis gas (50 sccm, 5% in He) and subsequent TPD. A detailed simulation methodology for the molecular dynamics simulations can be found in the ESI.

## **RESULTS AND DISCUSSION:**

The Fe@CNT and Fe@NCNT catalysts were synthesized via a single-step CVD decomposition of ferrocene dissolved in toluene (for Fe@CNT) or acetonitrile (for Fe@NCNT), as previously reported.<sup>42</sup> Comparison of these materials using Raman, TEM, XPS and XRD reveals clear nitrogen doping in the CNT support while maintaining a similar overall morphology. Raman spectra of both samples display sharp peaks at 1354 cm<sup>-1</sup> and 1597 cm<sup>-1</sup> (Fig. 1), which are assigned to the D and G bands, respectively. These are typically observed in the Raman spectra of CNT-based materials.<sup>43</sup> The D band becomes more intense as the number of defects in the sample



increases, and so the ratio of these peaks ( $I_D/I_G$ ) is often used as a measure of the overall order in a sample. Fe@CNT display a low  $I_D/I_G$  value of 0.2, while  $I_D/I_G$  for Fe@NCNT is much larger at 0.9. This increase in  $I_D/I_G$  is an indication of nitrogen incorporation in the CNT lattice, as the number of defects in the lattice increases due to poor assimilation of nitrogen atoms into the  $sp^2$  hybridized network.<sup>39, 43-48</sup> The final feature at ca.  $2666\text{ cm}^{-1}$  is the  $G'$  band, which is caused by two-phonon scattering processes that are free from the defect structures.<sup>49-51</sup> It is therefore suppressed in Fe@NCNT where defects are more prominent.

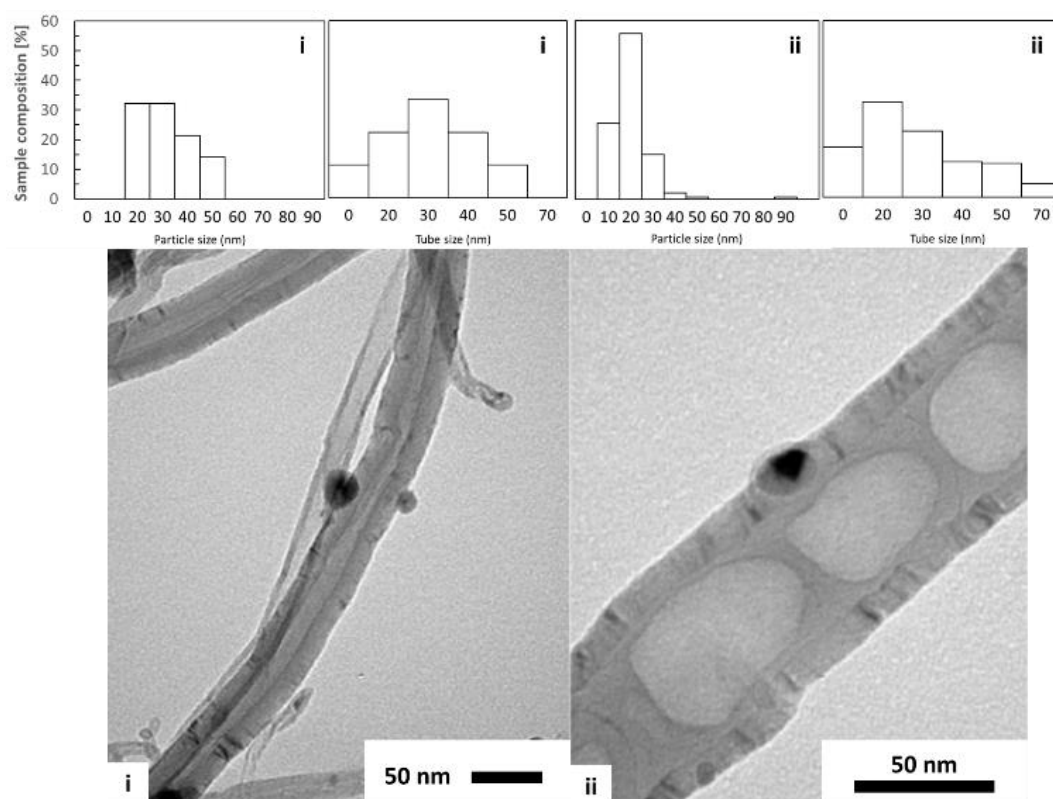


**Figure 1.** Raman spectra of Fe@CNTs and Fe@NCNTs after activation in air for 1 hour at 570 °C and 400 °C.

TEM analysis shows a similar morphology between the two materials, with a change in the internal bore structure attributed to the presence of nitrogen in Fe@NCNT (Fig. 2). In both cases, samples are composed of highly aligned bundles of nanotubes, with iron particles embedded into the CNT or NCNT support. In Fe@NCNT the average particle and tube diameters are  $25 (\pm 8)\text{ nm}$

and 35 ( $\pm 21$ ) nm, respectively, while Fe@CNT exhibit values of 34 ( $\pm 11$ ) nm and 35 ( $\pm 14$ ) nm. While these values are not identical, literature suggests that their activity and selectivity should be comparable, as particle size does not become a significant factor in FT catalysis until particle size decreases below 7 nm.<sup>52</sup> Fe@NCNT also display clear bamboo segmentation along the interior bore of the tubes. This is further evidence of nitrogen incorporation into the CNT lattice, as the previously discussed  $sp^2$  defects cause the lattice to deviate from the typical hollow CNT morphology observed in Fe@CNT.<sup>45-47</sup>

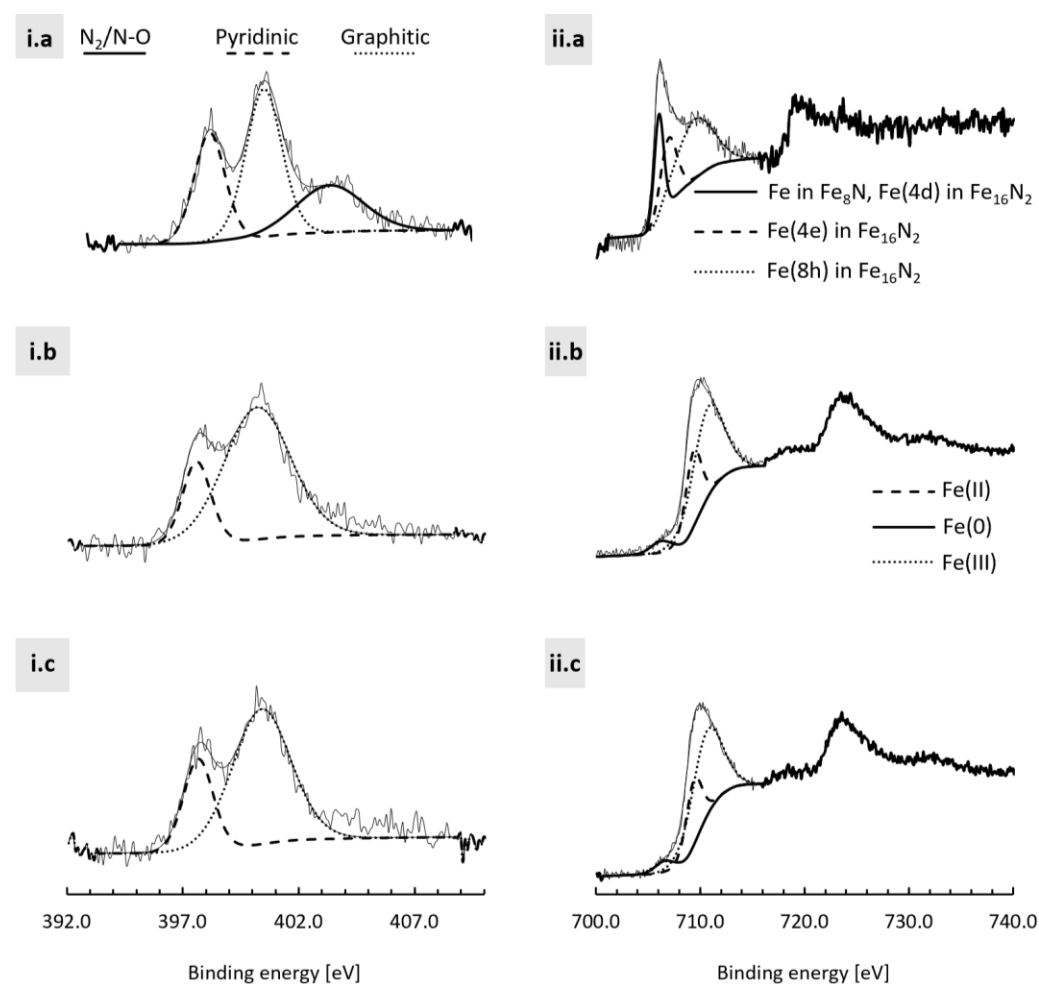
It is currently difficult to identify the origin of this difference in particle sizes despite largely identical synthesis conditions. In conventional supported iron nanoparticle catalysts, where the iron has been doped onto the catalyst surface via wet impregnation, nitrogen doping has been observed to improve dispersion and affect particle size by providing electron-rich anchoring sites for the nucleation and stabilization of metallic nanoparticles.<sup>11, 36, 39</sup> However, in Fe@CNT and Fe@NCNT the addition of iron nanoparticles is governed by the CNT growth mechanism during CVD synthesis rather than the mechanism of nanoparticle nucleation during wet impregnation. Because these residual particles are typically removed as impurities during commercial CNT production processes, the mechanisms and variables governing their formation remain unexplored and explanations for their different particle sizes remains a matter of debate. It is worth noting that the observed particle sizes are within the margin of error from each other. We therefore consider them as effectively similar for the purpose of this investigation.



**Figure 2.** TEM micrographs, particle and tube size distributions of (i)Fe@CNT and (ii) Fe@NCNT after activation in air for 1 hour at 570 °C and 400 °C.

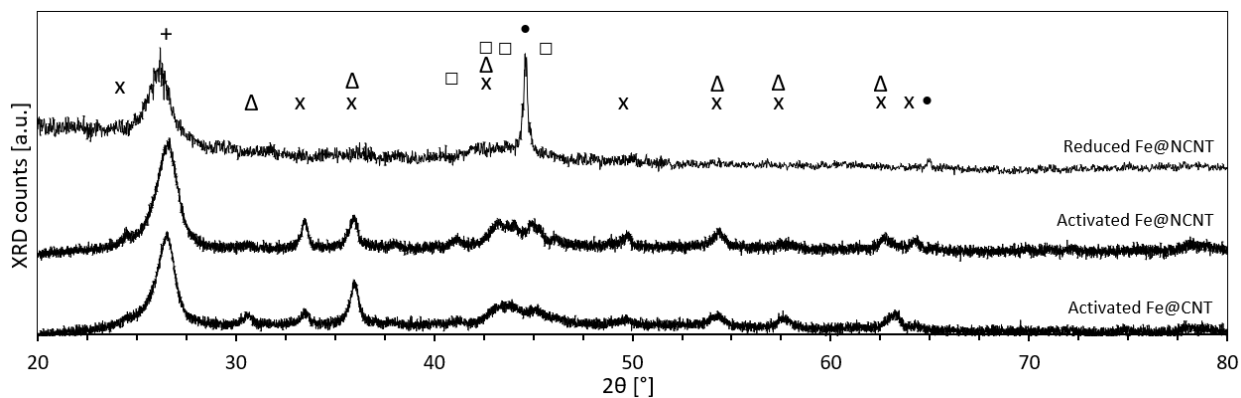
XPS spectra further confirm the presence of ca. 3 at. % nitrogen in the Fe@NCNT sample, with ca. 1 at. % iron exposed for catalysis in both Fe@CNT and Fe@NCNT after activation (SI, Table 1). Fe 2p spectra for Fe@NCNT (Fig 3.ii) suggests the formation of  $\text{Fe}_8\text{N}$  and  $\text{Fe}_{16}\text{N}_2$  after synthesis, as evidenced by peaks at 707.2, 708.0, and 710.5 eV.<sup>53</sup> These peaks shift to 707.5, 709.9, and 711.3 eV after oxidation in air to expose the iron particles for catalysis, suggesting the formation of Fe(0), Fe(II) and Fe(III) as a mix of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  and metallic iron, respectively.<sup>54-55</sup> A similar shift is observed for the iron carbides in Fe@CNT.<sup>34</sup> N 1s spectra for Fe@NCNT (Fig. 3.i) display peaks at ca. 398.8, 401.3, and 404.4 eV, corresponding to the presence of pyridinic, graphitic and physisorbed  $\text{N}_2$  or chemisorbed N–O species, respectively.<sup>39-</sup>

<sup>40, 43, 48</sup> These peaks initially appear at a ratio of 1:2:1 after synthesis, though this shifts to a ratio of 1:3:0 as the pyridinic, chemisorbed and physisorbed peaks are suppressed during the thermal activation process. This suggests that the nitrogen species in the CNT lattice consist primarily of graphitic nitrogen prior to catalytic testing. This may be significant, as different nitrogen environments have been noted to encourage different reactivity due to discrepancies in electron availability (e.g. graphitic nitrogen forms a shallow donor state, while the valence electrons in pyridinic and pyrrolic nitrogen sites remain confined to the  $\pi_z$  orbital).<sup>36, 39, 56</sup>



**Figure 3.** XPS spectra of (i) Fe@NCNT N 1s region (ii) Fe@NCNT Fe 2p region, (a) freshly synthesized, (b) activated at 400 °C in air for 1 hour, and (c) after a typical CO<sub>2</sub> reduction reaction.

pXRD further confirms similarities in the morphology and iron species of the two samples (Fig. 4). Both samples exhibit reflections at  $26.4^\circ$  corresponding to the CNT support structure. Reflections at  $30.5^\circ$ ,  $35.8^\circ$ ,  $43.4^\circ$ ,  $54.1^\circ$ ,  $57.6^\circ$ , and  $62.5^\circ$  confirm the presence of  $\text{Fe}_3\text{O}_4$  in both samples,<sup>57</sup> while reflections at  $24.2^\circ$ ,  $30.4^\circ$ ,  $33.3^\circ$ ,  $35.8^\circ$ ,  $41.0^\circ$ ,  $49.6^\circ$ ,  $54.1^\circ$ ,  $57.6^\circ$ ,  $62.5^\circ$ , and  $63.9^\circ$  confirm the presence of  $\text{Fe}_2\text{O}_3$ .<sup>58</sup> Iron carbides are also visible as a characteristic grouping of overlapping peaks between  $40^\circ$  and  $50^\circ$ .<sup>59</sup>  $\text{Fe@CNT}$  appear to have more intense reflections from  $\text{Fe}_2\text{O}_3$ , which is likely an effect of the higher activation temperature ( $T_{\text{act}}$ ) required to expose the iron particles for catalysis due to the greater thermal stability of the  $\text{Fe@CNT}$  ( $T_{\text{act}} = 570^\circ\text{C}$ ) compared to  $\text{Fe@NCNT}$  ( $T_{\text{act}} = 400^\circ\text{C}$ ).<sup>34</sup> Further justification of this difference in activation conditions can be found in the ESI. Beyond this difference, which is itself mitigated during catalyst reduction prior to catalysis,<sup>26</sup> pXRD suggests similar iron species between the iron particles of  $\text{Fe@CNT}$  and  $\text{Fe@NCNT}$ , with limited effect on the particles due to nitrogen doping. Reducing the  $\text{Fe@NCNT}$  sample results in suppression of the iron oxides and clear evolution of metallic iron characterized by reflections at  $44.9^\circ$  and  $64.9^\circ$ .<sup>60</sup> This is in good agreement with previous XRD studies of the  $\text{Fe@CNT}$  material.<sup>26</sup>



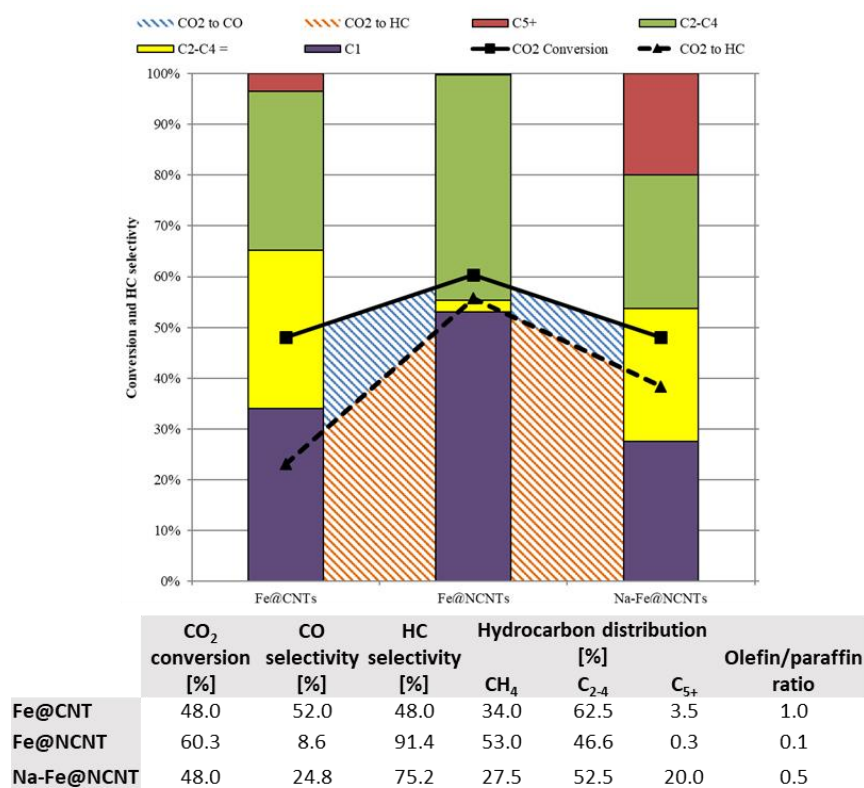
**Figure 4.** pXRD spectra of  $\text{Fe@CNT}$  and  $\text{Fe@NCNT}$  after activation at  $400^\circ\text{C}$  (or  $570^\circ\text{C}$  for  $\text{Fe@CNT}$ ) in air for 1 hour.  $\text{Fe@NCNT}$  after reduction in 50 sccm  $\text{H}_2$  at  $400^\circ\text{C}$  and atmospheric

pressure are also included. Spectra indicate the presence of the CNT support (+), Fe<sub>2</sub>O<sub>3</sub> (x), Fe<sub>3</sub>O<sub>4</sub> (Δ), iron carbides (□), metallic iron (•).

Despite similarities in morphology and iron species, Fe@CNT and Fe@NCNT perform notably differently when applied in catalytic CO<sub>2</sub> hydrogenation (Fig. 5). Fe@CNT result in lower overall conversion while favoring the production of CO, olefins and C<sub>n>1</sub> hydrocarbons. Nitrogen doping in Fe@NCNT appears to increase conversion of CO<sub>2</sub> and CO significantly, simultaneously shifting selectivity towards paraffins and methane. Nitrogen doping therefore appears to play a significant role in modulating the activity and selectivity of the catalyst. The reductive character of the iron catalyst may be enhanced through electron donation from the doped nitrogen, though this would be expected to increase activity without shifting product selectivity, or even enhance FT activity with additional C<sub>n>1</sub> formation rather than the significant increase in methane selectivity that is observed.<sup>39-40, 56</sup> Catalyst-support interactions have been maximized in both materials by integrating the catalytic iron particles directly into the CNT (or NCNT) support structure, and the catalyst compositions and morphologies appear to be largely identical aside from the nitrogen content of the support material itself. This suggests that additional mechanistic influences from nitrogen doping in the catalyst support (beyond just catalyst-support interactions) are affecting the outcome of the combined RWGS/FT process.

More specifically, the increased conversion, methane selectivity, and decreased CO selectivity in Fe@NCNT suggests that nitrogen doping serves to enhance RWGS activity and initial FT conversion into methane. At the same time, further reduction of C<sub>1</sub> FT intermediates into longer hydrocarbons via subsequent FT polymerization is disfavored. Interestingly, this trend appears to reflect an increased affinity for dipole-containing reactants (e.g. CO, CO<sub>2</sub>), while favoring the desorption of nonpolar products (e.g. short hydrocarbons). It is therefore possible that increased

attraction between the reactants and the catalyst increases their local concentration and serves to improve catalyst activity at the expense of long chain hydrocarbon formation. Similar effects have been reported for the enhanced adsorption of O<sub>2</sub> in the oxygen reduction reaction due to the presence of C–N dipoles and nitrogen environments in N-doped CNT and graphene catalysts.<sup>39, 61-62</sup> However, this effect has not been previously considered as a significant factor in RWGS or FT reactivity.

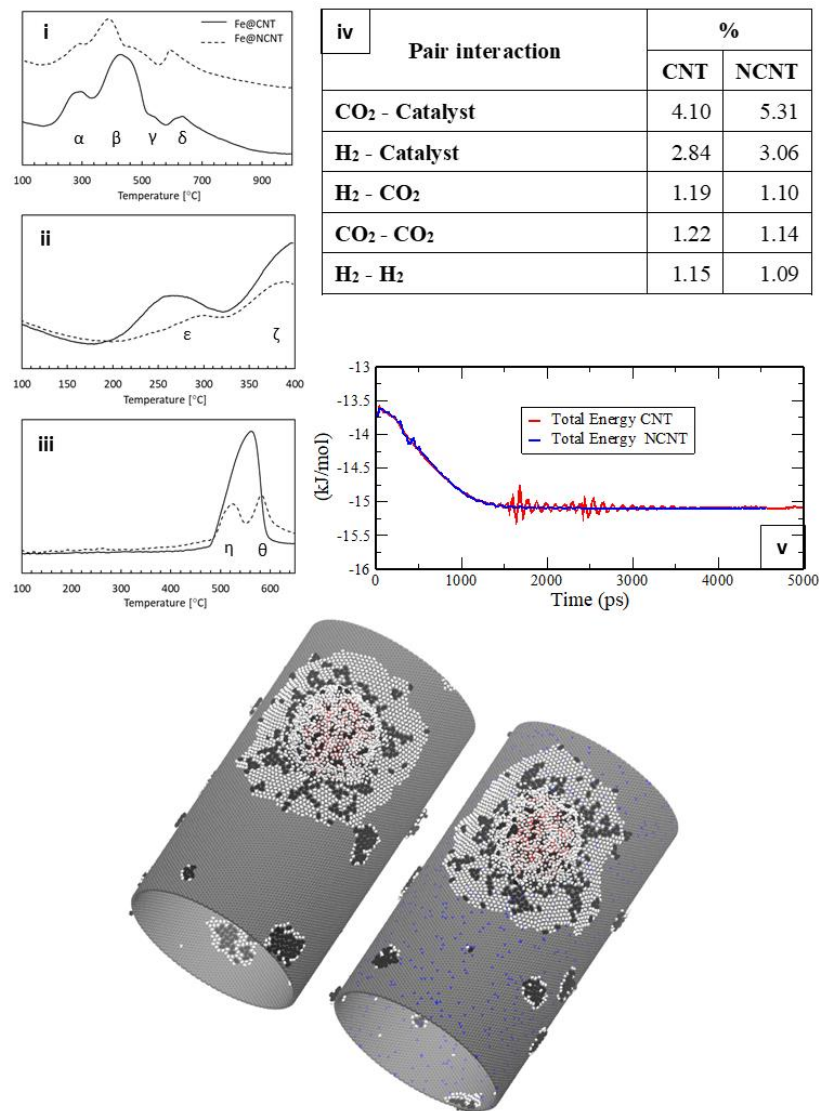


**Figure 5.** Effect of nitrogen doping on combined RWGS/FT reactivity at 370 °C, 15 bar, 8 scmm and an H<sub>2</sub>:CO<sub>2</sub> ratio of 3:1 using 0.4 g catalyst reduced in 50 scmm H<sub>2</sub> at 400 °C for 3 hours.

H<sub>2</sub> TPR, CO<sub>2</sub> and CO TPD spectra (Fig. 6.i-iii) indicate that Fe@NCNT are more easily reduced than Fe@CNT, as expected,<sup>11</sup> but also indicate that CO<sub>2</sub> and CO adsorb more strongly to the catalyst surface in Fe@NCNT. CO chemisorption has been observed to occur at ca. 400 °C over

Fe/CNT in literature.<sup>36</sup> Thus, peak  $\zeta$  has been attributed to chemisorbed CO and peak  $\epsilon$  has been attributed to physisorbed CO (Fig. 6.ii). While the desorption of chemisorbed CO appears largely unchanged between samples (ca. 395 °C), physisorbed CO desorbs at a notably higher temperature in Fe@NCNT. Stronger chemisorption by CO<sub>2</sub> at nitrogen sites is also observed in Fe@NCNT, where only physisorption is observed in Fe@CNT.<sup>36</sup> This increased attraction is mirrored in molecular dynamics simulations of the 3:1 H<sub>2</sub>:CO<sub>2</sub> feed gas adsorption process (Fig. 6iv). Interactions between CO<sub>2</sub> and the catalyst surface are notably stronger in Fe@NCNT, and a slight catalytic smoothing effect can be observed in the equilibration of reactants on the catalyst (Fig. 6.v). As CO<sub>2</sub> and CO are dipole-containing molecules, the C–N dipoles generated in the CNT lattice through nitrogen doping are likely sources of this enhanced attraction. Furthermore, it must be noted that the hydrocarbon products of this hydrogenation do not possess such dipoles, and are therefore at a relative disadvantage in terms of attraction to the catalyst compared to new CO<sub>2</sub> and CO reactant molecules. This can further influence their potential for chain lengthening by encouraging termination of the FT hydrogenation process via desorption after methane formation to facilitate coordination of new CO<sub>2</sub> and CO reactants.





**Figure 6.** (i) H<sub>2</sub> TPR, where  $\alpha = \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ ,  $\beta = \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}(0)$ ,  $\gamma = \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}(0)$  via FeO, and  $\delta =$  gasification of the CNTs. (ii) CO TPD, where  $\epsilon =$  physisorbed CO and  $\zeta =$  chemisorbed CO. (iii) CO<sub>2</sub> TPD, where  $\eta =$  physisorbed CO<sub>2</sub> and  $\theta =$  chemisorbed CO<sub>2</sub>. (iv, v) simulated 3:1 H<sub>2</sub>:CO<sub>2</sub> feed gas adsorption energies on Fe@CNT and Fe@NCNT. Detailed simulation methodology can be found in the ESI.

Sodium was doped onto Fe@NCNT via wet impregnation in an attempt to mask this effect by obscuring the nitrogen sites during catalysis via Na<sup>+</sup> coordination (Na-Fe@NCNT, Fig. 5). When

Na-Fe@NCNTs were tested in RWGS/FT catalysis, their behavior was observed to shift significantly back towards that of standard Fe@CNT, leading to reduced CO<sub>2</sub> and CO conversion, and increased olefin and C<sub>n>1</sub> hydrocarbon production. The slight increase in production of C<sub>5+</sub> hydrocarbons is likely an effect of the increased basicity caused by sodium doping, as has been previously observed.<sup>15</sup> Additional characterization of Na-Fe@NCNT is discussed in the ESI.

This further supports the hypothesis that nitrogen doping in CNT or graphitic supports for RWGS/FT hydrogenation does not only influence the process through increased interactions between the support and its catalytic nanoparticles. Moreover, the resulting C–N dipoles in the catalyst surface also play a significant role in determining the attraction of reagents to the catalyst surface. This increased attraction appears to enhance catalyst activity by increasing the local concentration of dipole-containing RWGS and FT reactants at the expense the formation of long-chain hydrocarbon formation. It is unclear whether the presence of different nitrogen species in the catalyst might result in a notably different outcome, though it should be noted that this effect may hold more strongly for materials in which graphitic nitrogen is most present. These findings suggest that while nitrogen doping can be a powerful tool in improving the performance of CO<sub>2</sub> and CO hydrogenation catalysts, it may be more preferably employed in materials intended for methanation rather than long-chain hydrocarbon production.

## ASSOCIATED CONTENT

### Supporting Information

Additional XPS characterization, full catalyst activation study to justify activation conditions, and detailed simulation methodology (PDF). Data created during this research are openly available from the University of Bath data archive at <http://dx.doi.org/10.5125/BATH-00616>

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Funding Sources

The authors would like to thank the UK Engineering and Physical Sciences Research Council (EPSRC) for their generous funding of this research.

## ACKNOWLEDGMENT

The authors would like to acknowledge the following entities for their critical contributions to this work: the Microscopy and Analysis Suite (MAS) at the University of Bath for their assistance and expertise in characterizing the described materials via Raman and TEM. The Material and Chemical Characterization Facility (MC<sup>2</sup>) at the University of Bath for their expertise in characterizing the described materials via TG-MS. Dr Gabriele Kociok-Köhn at the University of Bath Department of Chemistry for her expertise in characterizing the described materials via pXRD. The National EPSRC XPS Users' Service (NEXUS) at Newcastle University for their assistance and expertise in characterizing the underling Fe@NCNT materials via XPS.

## ABBREVIATIONS

FT, Fischer-Tropsch; WGS, water gas shift; RWGS, reverse water gas shift; CNT, carbon nanotubes; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy; pXRD, powder X-ray diffraction; TPD, temperature programmed desorption; CVD, chemical vapor deposition; SCCM, standard cubic centimeter; GC-MS, gas chromatography-mass spectrometry.

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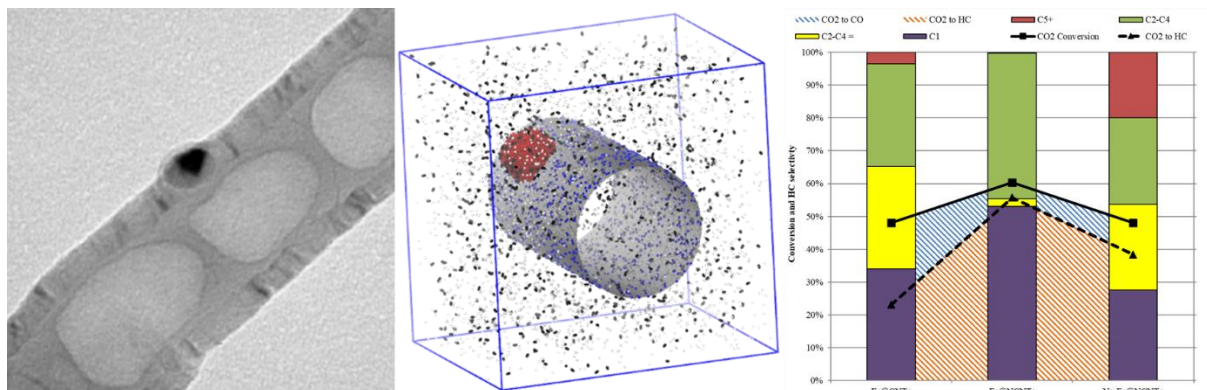
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C—N dipoles in a CO<sub>2</sub> hydrogenation catalyst result in increased reactant attraction, conversion, and a significant shift in products.